A Q-DLTS and transport study of graphene quantum dots in insulated matrix

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Deep level transient spectroscopy (DLTS) is a powerful method for study of a thermal activated emission of charge carriers from localized states in 2D films and multilayered structures. The widespread used conventional capacitance modification of the deep level transient spectroscopy technique (C-DLTS) was developed for uniform semiconductor structures and not for structures involving dielectric layers. In contrast, the Q-DLTS technique, which measures the charge (Q) rather than the capacitance, enables the characterization of traps (quantum-confinement levels) in complicated structures with insulated layers and quantum wells or quantum dots (QD) [1]. The latter is possible because the charge in measured structure shows considerable variations as traps in different layers of the structure undergo recharging while the capacitance is determined by the capacitance of dielectric layers. Q-DLTS in combination with temperature dependence of conductivity in the temperature range 80-300 K were used to characterize a 2D system with few-layer graphene QDs (thickness ~1 nm) imbedded in an insulating matrix of fluorinated graphene.

It was found that a few-minute treatment of graphene or few-layer graphene (FLG) in an HF aqueous solution led to strong changes in the structural and electrical properties of graphene samples involving a step-like increase in their resistivity (up to 10^{11} Ohm/□) [2]. Fluorination of FLG is suggested to occur during treatment of samples in HF aqueous solution. The process first proceeds at grain boundaries, and the strong increase in resistivity can be attributed to the formation of an insulating network blocking the conductivity in the graphene layer. The observed transformation of the network sample surface morphology into a nanoswell relief during longer HF treatments due to a self-organized corrugated process suggests the presence of graphene conductive islands (quantum dots) in the insulating matrix of functionalized graphene after the step-like increase of structure resistivity. The quantum dot size can be estimated as a half of nanoswell period. In this case QD sizes have to be equal to ~50-70 nm or smaller. The possibility of graphene quantum dot formation in a fluorinated graphene matrix was demonstrated in the theoretical study by Ribas et al. [3]. Formation of graphene quantum dots was also predicted for a corrugated graphene surface due to huge changes of the strain at nanometer scale [4].

Q-DLTS spectra exhibited one or two peaks in the temperature range 200 - 300 K (Fig.1a) with thermal activation energies E1 = 0.26 – 0.31 eV and E2 = 0.14 – 0.16 eV extracted from the Arrhenius plots (Fig.1b) (here, the energy values are given with statistical range of different measurements). The Q-DLTS measurements were performed by varying the time window τ_m while keeping the temperature unchanged. Here, the time window is $\tau_m = (t_2 - t_1)/\ln(t_2/t_1)$, where t_1 and t_2 are the times at which the Q-DLTS signal (due to the relaxation of the dielectric-trapped charge $\Delta Q = Q(t_2) – Q(t_1)$) was measured at the end of the filling pulse. Thus, the Q-DLTS measurements allowed us to extract one more important parameter, the time constant of carrier emission (electrons in our case) from observed levels. The carrier emission time for both levels was found to range from 0.5 to 35 ms in the temperature interval 200 – 300 K (see Fig.1a). Reference samples treated in HF aqueous solution for shorter times (before the increase of resistivity) displayed no peaks in their Q-DLTS spectra.

Current-voltage characteristics for different temperatures are shown in Fig. 2a. The considerable hysteresis was observed in the current values measured during different directions of voltage sweep. The voltages at which the current step was observed were almost identical (~7 - 8 V) in the temperature range 150 – 300 K. Arrhenius plots of the current values in the saturation region are shown in Fig. 2b. The activation energies extracted from those plots are E1* = 0.33 – 0.37 eV and E2* = 0.10 – 0.14 eV. Interestingly, roughly identical values of activation energies were obtained from Q-GLTS measurements and the temperature dependence of conductivity. It can be estimated from [5] that band gap 0.10 eV corresponds to QD size ~40 nm. This size of QD is good correlated with the expected QD size determined from period of the corrugated surface.

Interpretation of these activation energies and comparison of transport properties of investigated graphene layers with Q-DLTS results are discussed in the report.

Acknowledgements

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Figures

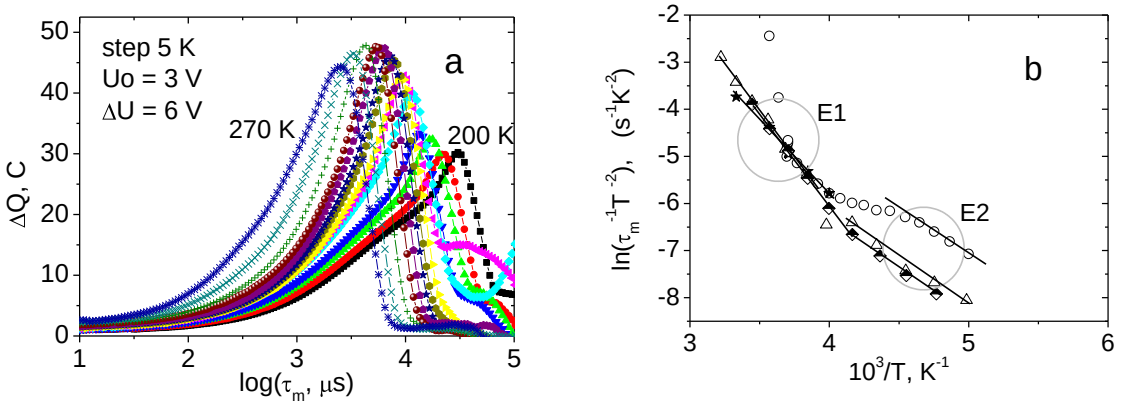

Fig.1. (a) Q-DLTS spectra for a sample of thickness ~1 nm treated in HF aqueous solution for 7 min. (b) Arrhenius plots extracted from repeated Q-DLTS measurements made on the same sample.

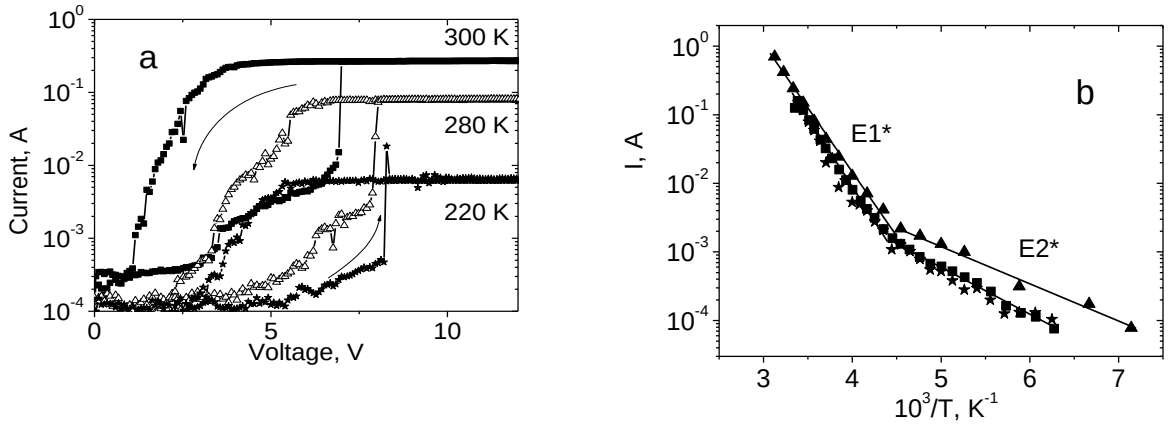

Fig.2. (a) Current-voltage characteristics measured with two directions of voltage sweep at different temperatures (b) Saturated current as a function of the reverse temperature.